Spring 5-31-1977

Analysis of combustion products of kynol and nomex

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ANALYSIS OF COMBUSTION PRODUCTS OF KYNOL AND NOMEX

BY

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A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN ENGINEERING SCIENCE

AT

NEW JERSEY INSTITUTE OF TECHNOLOGY

Newark, New Jersey
1977

APPROVAL OF THESIS

ANALYSIS OF COMBUSTION PRODUCTS OF

KYNOL AND NOMEX

BY

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FOR

DEPARTMENT OF CHEMISTRY

NEW JERSEY INSTITUTE OF TECHNOLOGY

BY

FACULTY COMMMITTEE

APPROVED: _____

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NEWARK, NEW JERSEY

OCTOBER, 1977

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ABSTRACT

The gaseous products generated by flaming combustion of Kynol and Nomex fibers under the same conditions (temperature 300-700°C, natural air) were quantitatively analyzed by infrared spectrophotometry, gas chromatography, mass spectrometry and a colorimetric tube method. The four techniques were chosen to examine the wide range of volatile and condensable products expected due to their different capabilities and sensitivities.

The main gases generated were carbon monoxide, carbon dioxide, methane and benzene.

The mass spectrometer was used to identify the condensed vapors. These were mainly phenol, methyl phenol and dimethyl phenol from the Kynol fiber and benzene, aniline, diamino-benzene, benzoic acid, benzonitrile, dicyanobenzene, diphenyl-amine and cyanophenylbenzene from Nomex. Ammonia and hydrogen cyanide were detected in small amounts from Kynol but in large amounts from Nomex. There was no indication of the presence of nitrogen monoxide or nitrogen dioxide in the combustion products of either fiber.

INTRODUCTION

The generation of the gaseous combustion products of synthetic polymers due to fire produces copious amounts of smoke and toxic gases, and thus possibly causes asphyxiation to humans trapped in the area of a fire. Concern is justifiably overdue. It is time to find out what kind of gases and liquid vapors are due to the combustion of these fibers in order to find a way to reduce death and injury due to fire. The two following types of heat resistant and inherently non-flammable fibers were selected to study the generation of these gaseous combustion products;

(1) Kynol-phenolic fiber (Carborundum Company), and

(2) Nomex fiber (DuPont Company).

The gaseous products generated by flaming combustion of Kynol and Nomex fibers under the same conditions (temperature 300-700°C, natural air) were quantitatively analyzed by infrared spectrophotometry, gas chromatography, mass spectrometry and a calorimetric tube method. The four techniques were chosen to examine the wide range of volatile and condensable products expected due to their different capabilities and sensitivities.

Kynol fiber is oriented to some extent.[8] This is produced from a melt-spun novolak phenol-formaldehyde resin, which is later further cross-linked with formaldehyde. It is, of course, legitimate to consider carbon fibers as extreme example of thermosets. Similarly, polyacrylonitrile can be cyclized and graphitized to form highly oriented carbon fibers.

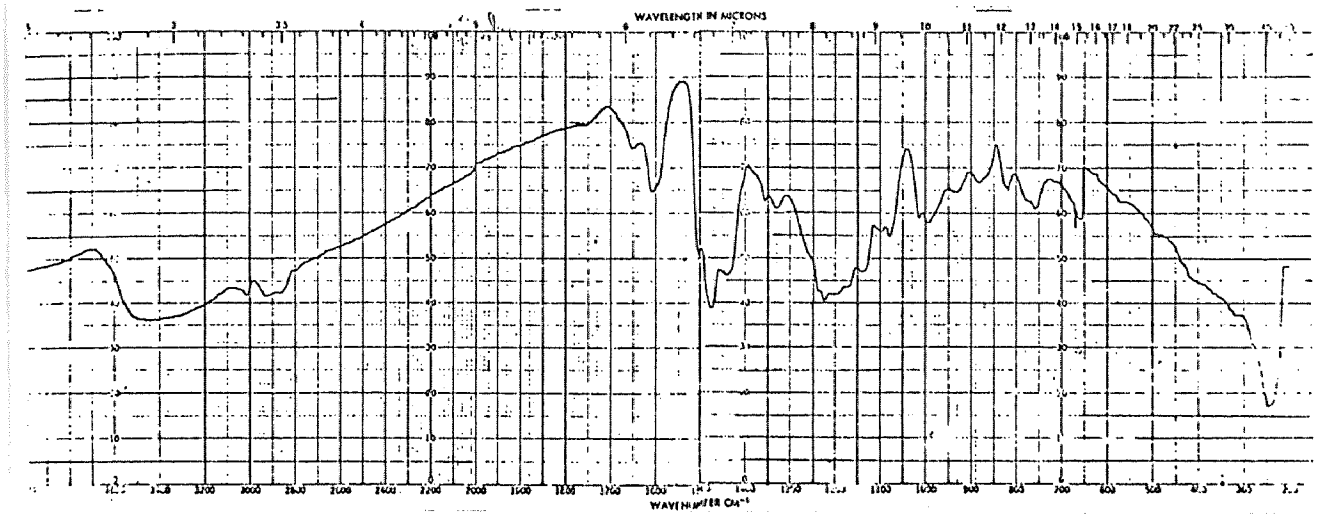


Fig. (1) The Infrared Spectrum of Kynol Fiber

Figure (1) shows the infrared spectrum of the Kynol fiber. The comfort feature of the Kynol fiber is due to the relatively high moisture regain of 6-7% which approaches values for cotton. The corrosion resistance, on the other hand, derives primarily from the stable cross-linked structure which minimizes attack and soiling by organic

solvent and tends to retard reaction with more corrosive acids and bases.[7]

Obviously, the reason for Kynol fiber's unusual flame resistance is related to the polymer structure which consists of phenolic units cross-linked with methylene units.

Aromatic polyamides, as basic constituents, contain either aromatic amino carboxylic acids or diamines and di-carboxylic acids, where the aromatic character may be in one or both constituents.[5] The polyamide from m-phenylene-diamine and isophthatic acid known as Nomex has found considerable interest as high-temperature resistant fibers. Figure (2) shows the spectra of Nomex which is characterized by the strong amide band at 1545 cm^{-1}.

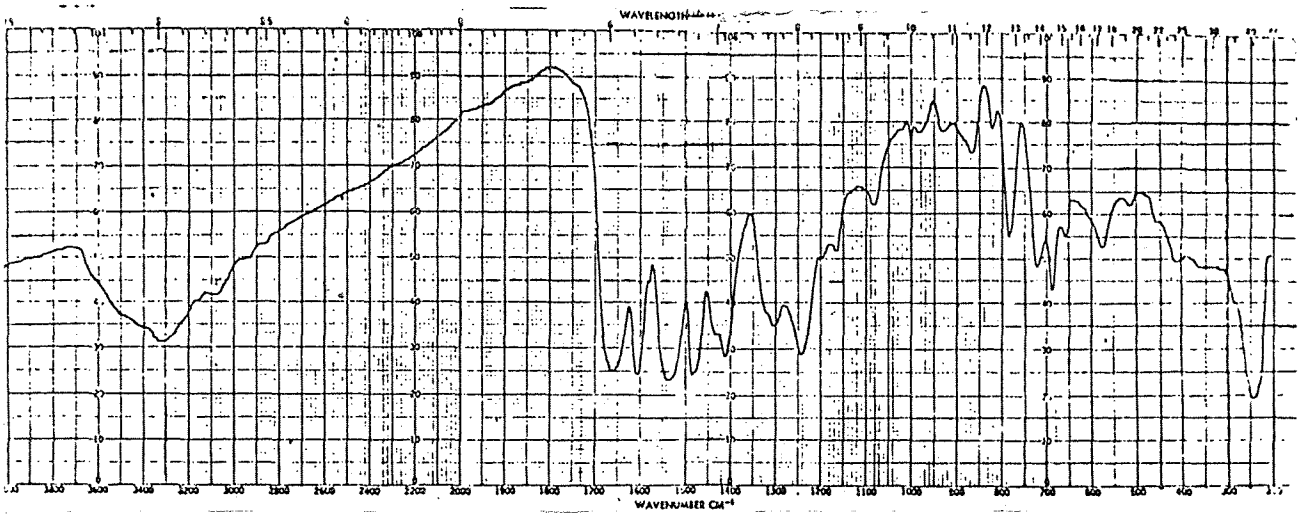


Fig. (2) The Infrared Spectrum of Nomex Fiber

Little is known on the crystal structure of these polymers, and nothing has been published on possible polymorphism. It is known that conjugation has a certain influence on the position of the amide bond I [V(c=o)].

Previous Work

Kynol fiber's unusual flame resistance is related to the polymer structure which consists of phenolic units cross-linked with methylene units. Thus, as indicated in equation I, Kynol fiber in a flame converts to a carbon fiber (60% yield) with evolution of CO_2, H_2O, and some CO. The concentration of CO depends on both the temperature and availability of air.[7]

$$\text{Kynol} \xrightarrow{\text{Flame}} \underset{(60\%\ \text{yield})}{\text{carbon fiber}} + CO_2 + H_2O + CO$$

Because of its cross-linking, Kynol fiber tends to convert to a glassy carbon type structure. The excellent shape retention of Kynol fiber in a flame can be attributed to at least two factors, namely, formation of a stable cross-linked structure during charring and the relatively high carbon yield. The flame resistance of Kynol fiber derives from several factors, which include the high carbon yield, absence of combustible gases, formation of a glassy carbon

surface with minimum surface for reaction and an ablative type cooling action from the formation of H_2O and CO_2. The stability of Kynol fiber to temperatures of even 2500°C in a torch is related to the excellent black body radiation characteristics which increase by the fourth power with increasing temperature.

There are some limitations of use of Kynol fiber under flame conditions. For example, in atmospheres containing 40% oxygen Kynol fiber will burn. Also extremely low density webs of Kynol fiber at densities less than 0.1 lb/ft^3 will flash in a flame. However, the carbon fibers which are produced still retain their shape. The flash is very likely due to the fact that sufficient oxygen is available to convert immediately all the Kynol fiber to carbon fibers. It is important to emphasize that Kynol fiber is not a high temperature fiber and, in fact, tends to degrade slowly at 200°C. Even at 150°C a slight oxidative instability has been detected in these fibers which indicates that 150°C represents the upper temperature limitation in air for long time use.

Kynol fibers have been examined under a number of high temperature conditions including inert and oxidizing environments, intermediate, and extreme temperature and short to

long periods of exposure. Under inert conditions the fibers display excellent thermal stability as shown in the isothermal data in Figure 3. For example, at 300°C the fibers show an initial weight loss of 5%, however, no additional loss can be detected even after 200 hours. At 400°C, the initial weight loss is 15% increasing slightly to 18% after 200 hours. At 1000°C a similar curve would be observed leveling out at about 40% weight loss. At 1000°C, the fiber has completely carbonized.

Because of the presence of hydrophilic hydroxyl groups, Kynol fibers display a higher moisture regain than is commonly observed in conventional synthetic organic fibers. The moisture regain is dependent on the fiber diameter of Kynol as shown in Table I, it increases with increasing surface area. At a denier of 1.0, the fibers display a moisture regain that is comparable to that of cotton. This factor contributes substantially to the excellent comfort characteristics which have been observed in Kynol wearing apparel. The fibers exhibit considerable resistance to wrinkling and provide a soft and pleasant touch to the skin.

TABLE I

Moisture Regain of Kynol Fibers

Relative Humidity	Moisture Regain %		
	4 Denier	2 Denier	1 Denier
40	2.3	3.6	5.5
65	4.2	6.0	8.4
100	15	18	22

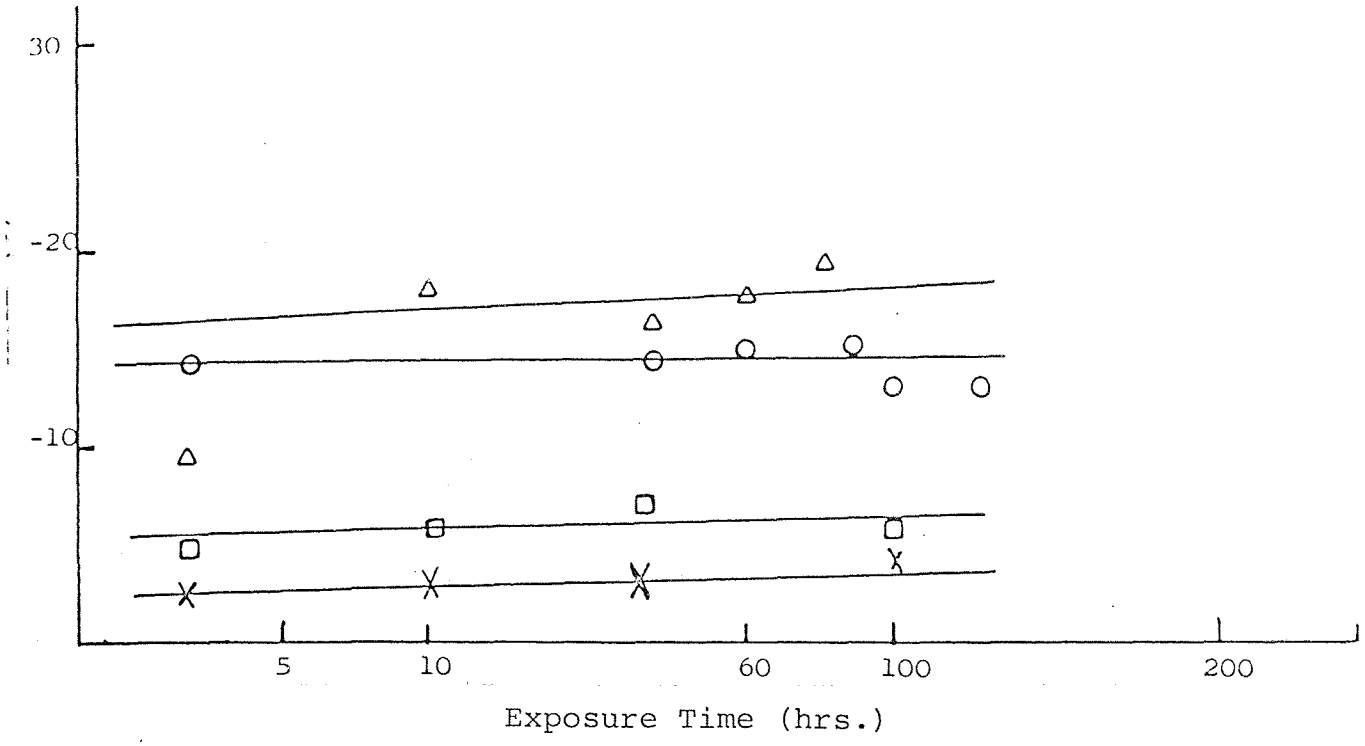


Fig. 3 Long Term Stability of Kynol in Nitrogen

Phenolic fibers display excellent resistance to non-oxidizing acids at room and elevated temperature. The fibers retain their integrity even when aged in concentrated sulfuric acid at 160°C for a week. In this treatment a weight increase of about 20% occurs due to partial sulfonation of the polymer. Concentrated phosphoric acid at 135°C does not affect the fiber integrity over a period of 5000 hours. The resistance of the fiber against dilute caustic and concentrated weak alkali is excellent. The fibers retain their original stress-strain properties when aged for three weeks in gaseous NH_3 at 150°C. Owing to their cross-linked nature, they are insoluble in all organic solvents up to their reflux temperature.[7]

The isothermal data may be somewhat misleading since differential thermal analysis of the Kynol fiber shows an endotherm at 100°C which changes to an exotherm at 140°C. The endotherm is due primarily to the evolution of adsorbed water and the incipient formation of small amounts of peroxide.[2] The exotherm at higher temperature is to a great extent dependent on the breakdown of these peroxides which occurs with evolution of heat. Based on the isothermal data it would appear that at any given time the percent of peroxide in the phenolic structure arising from oxidation is quite small. The presence of carbonyl, can be detected by infrared with exposure of the fiber to air

for five hours at 140°C. The intensity of this peak does not increase sharply with longer times at 140°C. This suggests that the carbonyl structure may be oxidizing further under these conditions so that the concentration of carbonyl is in a steady state. (Presumably the methylene bridges convert in a stepwise fashion to carbonyl and then to ether linkages.) Hence, the very small weight gain associated with carbonyl formation is compensated for by a corresponding weight loss.

The Kynol flammability properties were determined by the OI (Oxygen Index) and vertical flame test techniques.

The oxygen index is defined as the minimum volume concentration of oxygen required to support combustion of the specimen material (see Table II). The OI procedures were developed originally by the General Electric Company for determining flammability characteristics of polymer rods. Many variations can be introduced by the GE described procedure when testing textile structures. Such variables as fabric construction, fabric weight, moisture content, and finish can affect test results. Such factors as top or bottom ignition, conditioned or oven dried samples and wet or dry gas have bearing on the test results.[4]

TABLE II

Oxygen Index of
Knitted Fabrics

Fiber (100%)	OI
KYNOL	36.0
Verel	29.3
Nomex	28.1
PFR Rayon	27.0
Wool	21.6

The ignition temperatures and burning rates in ambient air (14.7 psia, 70°F, 65% RH) of treated cotton, spun Nomex and spun polybenzimidazole (PBI) fabric are given in Tables III and IV, respectively.[3] A preliminary determination of ignition temperature is made by holding a vertically oriented fabric test specimen against a calrod-type heater to which a thermocouple has been bonded and increasing the electrical power until fabric flaming is readily visible. The temperature of the surface of the heater at the instant before initiation of burning is the approximate fabric fire point. Additional tests are then made by preheating the calrod to temperatures above and below this level by means of a proportioning controller, moving the fabric test specimen against the heater and noting whether or not ignition occurs. The time from contact to initiation of burning is also noted. The ignition temperature is thus determined approximately within 50°F. This test procedure was developed originally for the

TABLE III
FABRIC IGNITION TEMPERATURE

Material	Calrod Temperature (°F) 1400	1450	1500	1550	1600	1650	1700	Ignition Temp (°F)
Cotton, flame-retardant treated	DNI 2 min*	I 5 sec	I 5 sec					1450
Spun Nomex		DNI 2 min		DNI 2 min	I 5 sec	I 5 sec		1600
Spun PBI				DNI 5 min	DNI 5 min	DNI 5 min	I 2 min	1700

DNI = did not ignite
I = ignited
* = approximate contact time of specimen with heat source.

TABLE IV
FABRIC BURNING RATE

Material	Ignition Method	End Ignited	Burning Rate (inch/sec)	Remarks
Cotton, flame-retardant treated	burning tissue	top	-	did not ignite
	burning tissue	bottom	-	charred surface but no apparent ignition; ignition may be masked by burning tissue flame
	Calrod	bottom	-	ignites and immediately self extinguishes
Spun Nomex	burning tissue	top	-	did not ignite
	burning tissue	bottom	0.61	self extinguishes after 20 sec; 3-4 inches of fabric burned
Spun PBI	either	either		does not burn

evaluation of fabric flammability characteristics because it simulates roughly the type of environment in which apparel must occasionally perform. In the laboratory test there is a variable temperature heat source (calrod heater) on one side of the fabric and heat sink (room temperature air) on the other.

As the data in Table IV shows, both flame retardant-treated cotton and Nomex fabric can be ignited and do burn in air. The PBI fabric does not burn in air.

The thermal conductivities of the fabrics were determined by the guarded hot-plate method. The test condition and results are given in Table V. Also given is the ratio of fabric thermal conductivity to thickness, i.e., the quantity of heat passing through the fabric per unit of fabric surface area per unit time per degree difference in temperature between the two fabric faces. As the results show fabric thermal conductivity increases with increasing temperature.

TABLE V

Fabric Thermal Conductivity

Material	Thermal Conductivity (Btu-inch/sw ft-hr-°F) at 70°F	at 500°F	Thermal Conductivity/Thickness (Btu/sw ft-hr-°F) at 70°F	at 500°F
Cotton, flame-retardant-treated, 4.5 oz/sq yd	0.39	--	40.2	--
Spun Nomex 5.0 oz/sq yd	0.29	0.45	22.3	34.6
Spun PBI 5.4 ox/sq yd	0.35	0.51	20.1	29.3

TABLE VI

Flammability Vertical Flame Test

Material	Weight (oz/sq yd)	Flame Time (sec)	Glow Time (sec)	Char Length (inches)
Hooker Treated Sage Green Cotton	5.0	0	0	4.0
Nomex, OG	3.3	0	12.8	3.2
Nomex, OG	5.0	0	15.2	3.4
PBI, Gold	3.0	0	0	2.3
PBI, Gold	5.0	0	0	0.6
Kynol	6.0	0	2.8	0.1

In Table VI, flammability data is presented for a number of fabrics.[6] It is interesting here to see how weight change results in an increase in glow time and char length for Nomex, while PBI char length decreases with increased weight. It is known that Kynol does not burn. However, the surface char continues to glow after removal of the flame source, even though the char length remains negligible. The pyrolysis of the Kynol fiber in helium produces CO_2 (m/e 44) and large amounts of water are released (m/e 18). When the resin decomposes, peaks at m/e 108, 107, and 94 appear. These indicate phenol and cresols are present. This means the combustion of the Kynol fibers in the natural air give almost the same kinds of gases and liquids as in helium environment.[1]

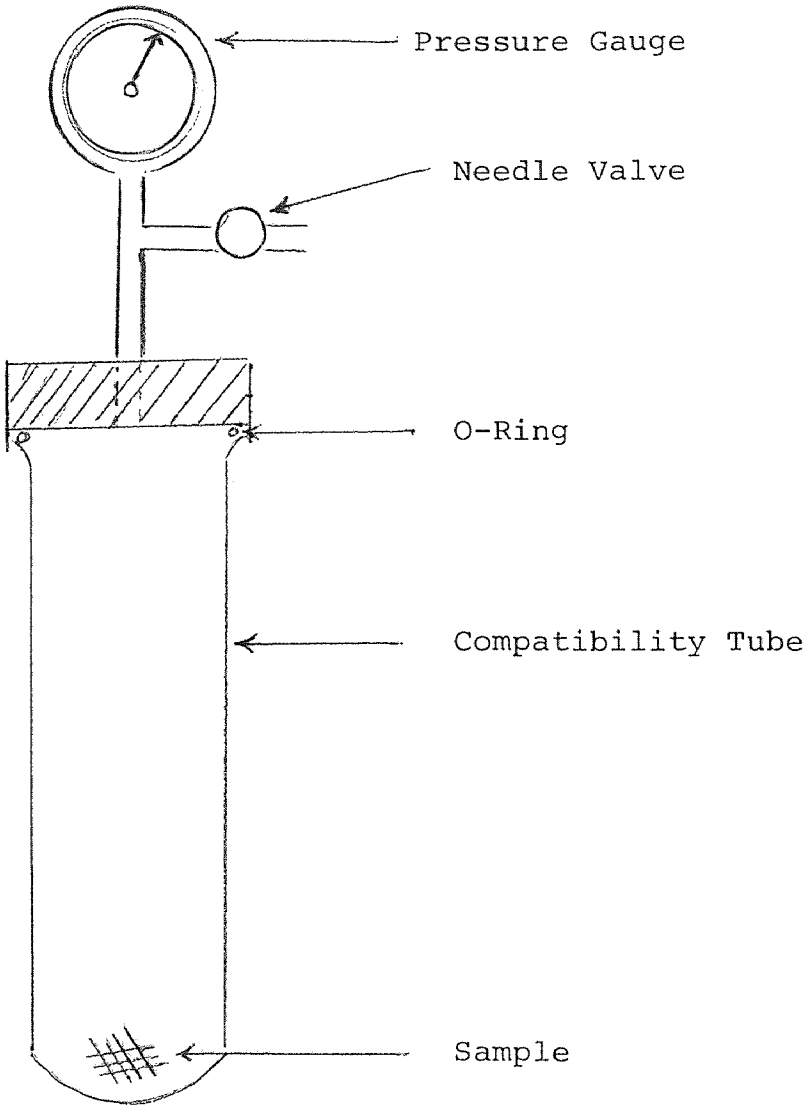
EXPERIMENTAL

I. APPARATUS

A three ounce compatibility tube with the protective coating removed (cat. #110-007 Laberest Scientific, a division of Fisher-Porter) was fitted with a Whiteg valve and a Matheson 300 lb/in^2 pressure gauge (Figure 3).

FIGURE 4

PYROLYSIS APPARATUS



II. METHOD

Approximately 10 grams of polymer fiber were placed into the compatability tube which contains approximately 100 ml of air at STP. The top was screwed on and the valve closed. The tube was heated with a Meeker burner flame until the pressure increased to 10 lb/in^2. The tube was allowed to cool to room temperature. The gaseous products were sampled for gas chromatography by syringe. (A septum was placed over the outlet and vacuum was created in the space between the septum and the valve. The space was then flushed once with the sample gas before the sample was removed by syringe.)

The gases were also analyzed by mass spectrometry through the cold inlet on an A.E.I. Ms902 mass spectrometer. A 70eV spectrum was recorded. The compatibility tube was attached to the cold inlet of the mass spectrometer. The air between the needle valve and inlet was pumped out. The valve was opened and the gases were introduced into the mass spectrometer through a sintered glass leak. The spectrum obtained showed that the oxygen, O_2, had been used completely in combustion. The presence of methane, CH_4, was ascertained from the relative intensity values of m/e 16, 15, 14, 13, and 12 that were identical to the spectrum of a known sample of methane. Carbon dioxide was observed at m/e 44, while CO cannot be observed because of the interference of nitrogen and the fragmentation of CO_2 giving m/e 28.

A condensate formed at the top of the compatability tube near the gas outlet where the tube was near the room temperature. Several droplets of this condensate were absorbed into a piece of ceramic thermocouple tubing which was then placed on the probe of the mass spectrometer. A 70eV spectrum was taken from probe temperature of 25°C to 200°C. The compounds were introduced into the mass spectrometer as the temperature of the probe was increased. Each component was identified by its molecular ion.

Infrared

The gas samples shown below were scanned in a Beckman Model 12 Infrared spectrophotometer using a slit width of four (4) reciprocal centimeters and an energy rate of 1:1 SB/DB. The calibration of the infrared spectrophotometer was performed in the following manner:

A 10 cm path length cell was evacuated to 10^{-3} torr and a background spectrum obtained. High purity nitrogen, 300 torr pressure, was then added to the cell and the background again checked. The carbon monoxide was then added in 100 torr increments and the spectrum scanned between additions. The adsorbance versus concentration curve was plotted and used to analyze the combustion products (Table VII).

All spectra were obtained under identical instrument conditions.

TABLE VII
CARBON MONOXIDE INSTRUMENT CALIBRATION

Carbon Monoxide Pressure	Carbon Monoxide Calibration Adsorbance at 2172 cm^{-1}
100 torr	0.068
200 torr	0.134
300 torr	0.200
400 torr	0.268

Colorimetric Tube Analysis (Drager Tube)

Some of the trace gases produced during combustion are not detectable due to instrumental limitations. Colorimetric tubes (Drager tube: New Jersey Safety Equipment Company) having detection ranges to 70 parts per million were used.

The Drager tube uses the following principle of operation. The ammonia 5/a tube is an acid orange indicating layer containing bromophenol blue reagent that changes to the dark blue ammonia salt. A standard volume of air is pumped through the calibrated tube leading to color development length being equal to reactant concentration.

Possible interfering compounds are:

(1) hydrazine and t,1-dimethylhydrazine. If these were present the M.S. should detect them.

(2) substituted amines. The sensitivity of this system would be very different from ammonia.

The hydrogen cyanide tube uses similar mechanical principles but chemically the reaction is:

$$HCN + HgCl_2 \longrightarrow HCl + Hg(CN)_2$$

$$HCl + \text{Methyl red} \longrightarrow \text{red reaction product}$$

Most interfering gases (H_2S , SO_2, NO_2 and NH_3) are eliminated by a precleaning layer incorporated in the detection tube.

RESULTS

Gas Chromatography

Gas chromatographic identification was accomplished by comparing relative retention time of unknowns with known materials and by peak augmentation of the known material into the combustion gases. Air supplied known samples of N_2 and O_2 powdered Dry Ice was placed in a small jar. The CO_2 displaces the air and gives a good known sample for CO_2. Lecture bottles of Matheson CO and CH_4 were used for these known samples. The peak augmentation experiments were done by using a "piggyback" injection technique. The sample was drawn into the gas syringe then the known was drawn into the same syringe in "piggyback" fashion. The total gas mixture was injected into the G.C. If the peak increase in peak height without any observable shoulders or other peaks, then the material was identified as the known substance used in the experiment. This technique identifies low molecular weight gases to a high degree of confidence. The retention times of these gases are given in Table VIII.

TABLE VIII

PORAPAK P COLUMN

Programmed at room temperature to 200°C, @15°/min. starting at ambient temperature

Compound	Retention Time
air	0.2 min
CO	0.6 min
CH_4	3.2 min
CO_2	8.6 min

A. KYNOL

The expected combustion products of carbon dioxide, carbon monoxide, and water were observed. Methane was also observed. We believe methane to be a product of pyrolysis.

B. NOMEX

The expected combustion products of CO_2, CO, and water were formed again. Some benzene was also observed as product of incomplete combustion.

Mass Spectrometry

A. KYNOL

The gases identified by gas chromatography were verified by mass spectrometry. We also observed the following compounds in the liquid condensate:

1. Phenol $M.^+ = 94$
2. Methyl Phenol $M.^+ = 108$
3. Dimethyl Phenol $M.^+ = 122$

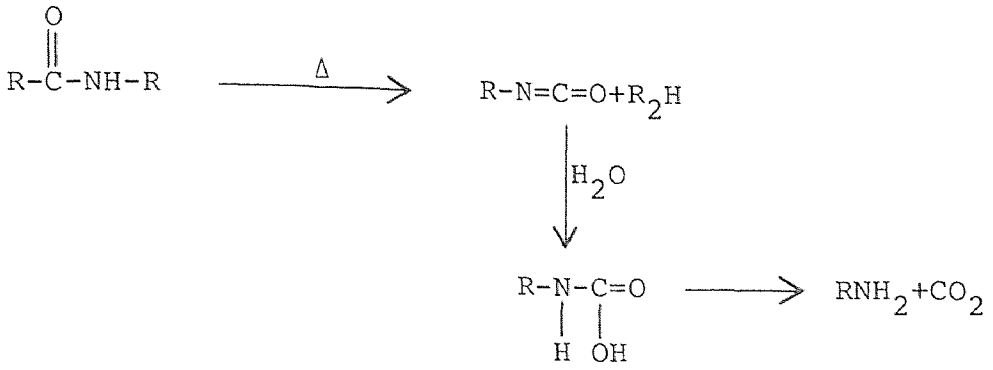
These products were probably formed by pyrolysis of the fiber.

B. NOMEX

Besides verifying the G.C. analysis we observed spectra for the following compounds in liquid condensate:

1.	Benzene	$M.^+ = 78$
2.	Aniline	$M.^+ = 93$
3.	Diamino benzene	$M.^+ = 108$
4.	Benzoic acid	$M.^+ = 122$
5.	Benzonitrile	$M.^+ = 103$
6.	Dicyanobenzene	$M.^+ = 128$
7.	Diphenylamine	$M.^+ = 169$
8.	Cyanophenylbenzene	$M.^+ = 179$
9.	3 Other Compounds	$M.^+ = 130, 148, 173$
10.	Solvent (N,N-Dimethyl acetamide)	$M.^+ = 87$

Most of those compounds are probably formed by pyrolysis of fiber, in some cases followed by hydrolysis. Pyrolysis of the polyamide might form isocyanates. Water is present in the tube from the original air in the tube as well as that which is formed by combustion. Isocyanates react readily with water to form compounds that decompose at room temperature to amines and CO_2 (Scheme 1).



Infrared

The following assignments and concentrations were determined:

Component	Wavelength (cm^{-1})	Kynol Fiber Concentration (mm Hg)	Nomex Fiber Concentration (mm Hg)
Carbon Monoxide	2172	240	136
Carbon Dioxide	2362	54	41
Methane	3019	23	9
Methanol	1030	4	Not Detectable
Benzene	672	Not Detectable (<0.01)	0.06
Ammonia	960	Not Detectable (<0.1)	0.4
Water		Uncalibrated	0.1

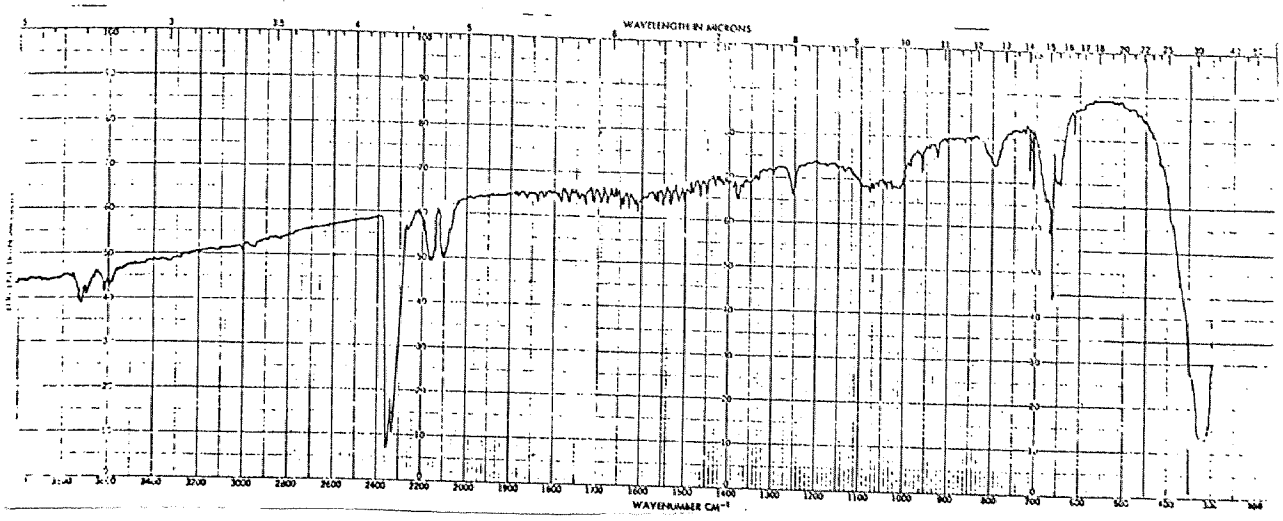


Figure (5) The infrared spectrum of the gaseous combustion products of Nomex.

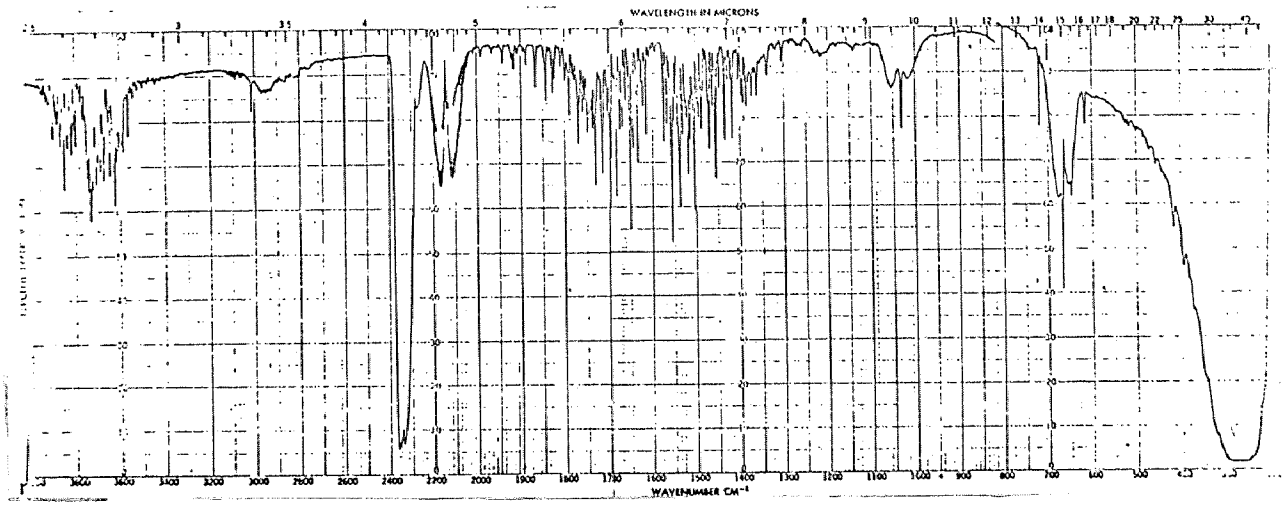
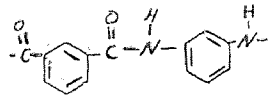


Figure (6) The infrared spectrum of gaseous combustion products of Kynol.

Colorimetric Tube Analysis (DRAGER Tube)

Colorimetric tubes (DRAGER tube: New Jersey Safety Equipment Company) having detection ranges to 70 parts per million were used with the following results:

	NH_3	HCN	NO	NO_2
Kynol	20 ppm	5 ppm	NONE	NONE
Nomex	>70 ppm	>30 ppm	NONE	NONE

The nitrogen products are greater in the Nomex fiber combustion since Nomex fiber contains two nitrogen per repeat unit ()$_n$, while Kynol only has the residual surface amines after treatment with ammonia.

CONCLUSION

The gaseous products generated by flaming combustion of Kynol and Nomex fibers under the same conditions (temperature 300-700°C, in air) were quantitatively analyzed by infrared spectrophotometry, gas chromatograph, mass spectrometer and a colorimetric tube method. These four techniques were chosen to examine the wide range of volatile and condensable products because of the differences in capabilities, limitations, and sensitivities of each method used. Combustion of Kynol and Nomex produces copious amounts of smoke and toxic gases which could cause asphyxiation to people trapped in the area of a fire.

The most interesting observation in this work is that certain toxic gases (hydrogen cyanide, carbon monoxide, and ammonia), were evolved as combustion products from both Nomex and Kynol fibers. However, the amounts of nitrogenous compounds (HCN, NH_3) liberated from Nomex were considerably more than that from Kynol. This is because nitrogen is present in each repeating unit of the Nomex polymer backbone. On the other hand the nitrogen compounds from Kynol are due to chemicals introduced during the after-treatment rather than originally present in the polymer itself. Comparison of the I.R. and G.C. analysis indicate that methanol and ammonia were identified by the I.R. rather than the G.C. technique.

Partially decomposed organic molecules were identified by using the M.S. method while other smaller molecules were analyzed by the other three analytical tools mentioned above. Thus, a combination of all these analytical methods provides a more complete picture of the combustion products than any single method can.

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